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Application of potentiometric stripping analysis with constant inverse current for determining soluble lead in human teeth

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Abstract

A method for the determination of soluble lead in human teeth by potentiometric stripping analysis with constant inverse current in the analytic step (PSA-i_R), is described. The metal ions were concentrated as their amalgams on the glassy carbon surface of a working electrode that was previously coated with a thin mercury film and then stripped by a suitable oxidant. This paper examined effect of various factors on the PSA-i_R results including the electrolysis potential, the solution stirring rate, and the constant inverse current. Quantitative analysis was carried out by both standard addition and calibration curve methods; a good linearity was obtained in the concentration range from 5 to 25 μg/dm^3. A detection limit of 0.64 μg/dm^3 was obtained, with a 5.21% coefficient of variation. Results obtained for teeth were not significantly different from these obtained by flameless atomic absorption spectrophotometry (FAAS).

Keywords: Potentiometric stripping analysis; Constant inverse current; Lead; Teeth

1. Introduction

Lead is an ubiquitous very toxic element, the impact of which on the environment has been extensively reviewed [1]. It is well known that profound biochemical and neurological changes can be caused by even small quantities of lead [2]. Continuous exposure to low lead levels results in its accumulation and retention in the human body, and elevated concentrations of this heavy metal are observed in many tissues [3]. The earliest effects of lead intoxication are observed in the hematopoetic system, on peripheral nerve conduction, and possibly on higher nerve function in children. Other points of attack include kidneys, gastrointestinal system, brain, gingival tissues, and embryo [1,3]. This heavy metal is also accumulated in calcified tissues, like bone and teeth [4]. Several studies have shown that human teeth may be valuable indicator of past exposure to such heavy metals, because of their physical stability. Teeth are also a readily accessible biological tissue for the analysis [5–7].

Regarding the fact that the toxic and catalytic effect of some metals also becomes manifested at the contents lower than 1 mg/kg [8], only a few instrumental techniques are capable for their determination at that level like neutron-activation analysis, atomic absorption spectrophotometry, plasma-emission spectrometry and electrochemical stripping analysis (ESA). The detection limit, selectivity and reproducibility, high throughput and simplicity of electrochemical stripping analysis as well as the price of the device give it some priority [9,10].

In this work potentiometric stripping analysis was modified to include constant inverse current in the analytic step (PSA-i_R).

The superposition of constant inverse current in the analytic step has a double effect: it leads to the reduction of the already oxidized deposit as well as to the reduction of the oxygen content in the vicinity of the working electrode [11,12]. Application of this technique considerably increases the sensitivity of the lead determination because the oxidation rate of the deposit is reduced along with the concentration of oxygen. The value of the reduction current must be selected to ensure that the oxidation rate is greater than the rate of reduction [13].

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The aim of this study was to define a method for the determination of soluble lead in human teeth by applying potentiometric stripping analysis with constant inverse current in the analytic step (PSA-i_R) [14]. In order to carry out the assigned task a great number of sample preparation procedures was examined and the corresponding conditions for the lead PSA-i_R analysis defined.

2. Experimental

2.1. Chemicals and solutions

Glacial acetic acid (p.a. grade), hydrochloric acid (suprapur grade), standard solution of lead (1 g/dm^3, "Titrisol"), and standard solution of mercury (1 g/dm^3, "Titrisol") were purchased from Merck (Darmstadt, Germany) and have been used as received. Working solutions were prepared by the dilution of standard solution with doubly distilled water.

All containers, vessels and cells were washed with nitric acid (1:1) and doubly distilled water before used.

2.2. Instrumentation

The stripping analyzer M1 produced by Elektrouniverzal, Leskovac, and the Faculty of Technology, Novi Sad, is a highly automatic instrument for potentiometric and chronopotentiometric stripping analysis with microprocessor control of the complete process [15]. The analyzer has a program for automatic qualitative and quantitative determination, including the calculation of element contents. The instrument can be programmed to give deposition potentials between −2 and 2 V and a constant current for the electrolysis or stripping step between −50 and 50 μA, with the parameter setting accuracies $\Delta E < 2$ mV and $\Delta i < 0.2$ μA. Flameless atomic absorption spectrophotometry (FAAS) measurements were carried out with Perkin Elmer 1100 AAS spectrophotometer.

For the lead determination by FAAS the following five-step procedure was adopted:

1. Drying of sample for 30 s at 150 °C with temperature ramp up time of 10 s.
2. Sample mineralization for 5 s at 850 °C with temperature ramp up time of 5 s.
3. Sample atomization at 1800 °C (instanly reached) with integration time of 3 s.
4. Cuvette cleaning at 2500 °C for 1 s with temperature ramp up time of 1 s.
5. Cooling of the cuvette for 10 s at 20 °C with temperature ramp down time of 5 s.

Hollow cathode lamp with 217.00 nm wavelengths was used as a radiation source. The argon flow rate through the graphite cuvette was 300 cm^3/min. Sample volume for all analyses was 20 mm^3.

2.3. Electrochemical cell and electrodes

The electrochemical cell consists of a process vessel bowl, an electromagnetic valve, a Teflon mechanical stirrer (1000–6000 rpm) and a three-electrode system. A glassy carbon (SIGRADUR-G) working electrode with 7.07 mm^2 total surface area was pressed into a Teflon tube (outer diameter 8 mm) at an elevated temperature. An Ag/AgCl, KCl (3.5 mol/dm^3) electrode was used as the reference and a platinum wire as counter electrode [11].

2.4. Preparation of the working electrode

A thin layer mercury electrode on glassy carbon as an inert support was used. Before electrode formation, the glassy carbon surface was swept with filter paper first soaked with acetone and then with doubly distilled water. The mercury film was formed electrolitically from a solution containing 100 mg/dm^3 mercury (II)-ion and 0.02 mol/dm^3 hydrochloric acid at a constant current of 50 μA for 240 s [10].

2.5. Sample preparation

The teeth analyzed in this study were all permanent teeth of adult persons obtained from University Dental Clinic in Niš. Both caries-free teeth extracted from orthodontic reasons and teeth with amalgam filling have been investigated. After extraction teeth were cleaned with a polyethylene scraper and then rinsed with saline solution and finally with doubly distilled water. Cleaned teeth were dried 6 h at 60 °C and then crushed to small pieces (approximately 2–3 mm) with pliers. Prepared teeth were treated with 100 cm^3 of 4% acetic acid for 24 h (±10 min) at 22 ± 2 °C. Obtained solutions were used for lead determination without further dilution because acetic acid served as a supporting electrolyte.

Amalgam filling was mechanically removed from one tooth, which was then treated the same way as caries-free teeth.

3. Results and discussion

3.1. The PSA-i_R of lead

In order to determine the optimal conditions of the PSA-i_R of lead in 4% acetic acid solution the effects of electrolysis potential, solution stirring rate, and inverse current were examined. After conditions optimization the linearity of the analytical signal (oxidation time-τ_{ox})and the detection limit were defined.

3.2. The electrolysis potential

In order to define the optimal electrolysis potential, potentials from −0.80 to −1.10 V with respect to 3.5 mol/dm^3 Ag/AgCl, KCl were examined. Solutions with

Table 1
The reproducibility of the oxidation time (τ_{ox}) expressed as the variation coefficient (C_V) for different electrolysis potentials (E)

E (V)	Pb concentration			
	5 μg/dm^3		15 μg/dm^3	
	τ_{ox} (s)	C_V (%)	τ_{ox} (s)	C_V (%)
−0.80	0.19	3.71	0.41	5.00
−0.85	0.23	4.60	0.42	6.28
−0.91	0.25	3.76	0.40	5.18
−0.96	0.27	1.12	0.47	2.73
−1.01	0.29	5.23	0.46	3.93
−1.06	0.32	4.58	0.44	4.97
−1.10	0.35	3.95	0.38	5.45

5 μg/dm^3 and 15 μg/dm^3 of lead were analyzed at the electrolysis time of 300 s (5 μg/dm^3) and 180 s (15 μg/dm^3) and an inverse current of 2 μA.

The reproducibility of the oxidation time (τ_{ox}) expressed as the variation coefficient (C_V) for different electrolysis potentials (E) is presented in Table 1.

The best reproducibility expressed as the coefficient of variation was achieved at −0.96 V for both 5 μg/dm^3 (1.12%) and 15 μg/dm^3 (2.73%) solution of lead. The electrolysis potential of −0.96 V was there fore used for all the subsequent analysis.

The lead dissolution potential (qualitative characteristic) was always around −0.42 V independently of the electrolysis potential. Regarding the close values of dissolution potentials of Pb, Tl, and Sn (−0.46, −0.46, and −0.49 V versus SCE, respectively) there is a possibility for overlapping of their analytical signals. However, the AAS analysis of our samples (acetic acid extracts of teeth) did not show the presence of neither Tl or Sn.

3.3. The stirring rate of the solution

The stirring rate of the solution was examined at the values of 1000, 2000, 4000 and 5000 rpm of a Teflon rod stirrer. Solution stirring rate of 6000 rpm caused the mercury layer peeling from the glassy carbon electrode surface. The optimal stirring rate was 4000 rpm with the analytical signal variation coefficient of 2.8 and 3.2%, for a lead content of 5 and 15 μg/dm^3, respectively. For all subsequent experiments, the stirring rate of 4000 rpm was adopted.

3.4. The constant inverse current

The effect of the constant inverse current on the analytical signal of lead (τ_{ox}) for a lead content of 5 μg/dm^3; (electrolysis time of 300 s), and 15 μg/dm^3; (electrolysis time of 180 s) on the reproducibility expressed through the coefficient of variation is presented in Table 2.

The optimal value of the inverse current for a lead content of 5 μg/dm^3 was 1.6 μA with a reproducibility of 2.33%, while for a lead content of 15 μg/dm^3 the optimal inverse current of 1.2 μA with a reproducibility of 4.21% was determined.

Table 2
The reproducibility of the analytical signals (τ_{ox}) expressed through the variation coefficient (C_V) for the different values of constant inverse current (i_R)

i_R (μA)	Pb concentration			
	5 μg/dm^3		15 μg/dm^3	
	τ_{ox} (s)	C_V (%)	τ_{ox} (s)	C_V (%)
0.5	0.48	7.42	0.55	7.62
1.2	0.52	3.65	0.84	4.21
1.6	0.87	2.33	1.28	5.44
2.0	1.53	8.57	2.31	8.10

3.5. The linearity of the analytical signal

The linearity of the analytical signal of the lead PSA-i_R was examined for the mass concentrations in the range from 5 to 25 μg/dm^3 at an electrolysis potential of −0.96 V, electrolysis time of 300 s, a solution stirring rate of 4000 rpm and an inverse current of 1.2 μA. Good linearity ($r > 0.990$) was obtained in the range of concentrations examined. The analytical signal (τ_{ox}) dependence on the lead concentration (C_m) obeyed the following equation:

$$\tau_{ox} = 0.462 + 0.021 \cdot C_m;\ (r = 0.998)$$

3.6. The detection limit

The detection limit of the PSA-i_R of lead was 0.64 μg/dm^3 for an electrolysis time of 600 s at an electrolysis potential of −0.96 V, with a stirring rate of 4000 rpm and an inverse current of 2 μA.

Good reproducibility was obtained with $C_V = 5.21\%$.

For lower lead contents it was necessary to apply a larger inverse current and that is why an inverse current of 2 μA was applied for the detection limit determination.

3.7. The PSA-i_R of soluble lead in teeth

On the basis of the above examinations, a method for the determination of the soluble lead in human teeth using potentiometric stripping analysis with constant inverse current in the analytic step (PSA-i_R) was defined. The defined method was applicable for the analysis of samples (extracts of human teeth with 4% acetic acid as the extractant and supporting electrolyte) on a thin layer mercury electrode on glassy carbon as an inert support. The mercury layer had been formed at a constant current of 50 μA and a deposition time of 240 s. The inverse current was 1.2 μA, the stirring rate was 4000 rpm, the electrolysis potential was −0.96 V versus Ag/AgCl, KCl (3.5 mol/dm^3), and the electrolysis time was 240 s.

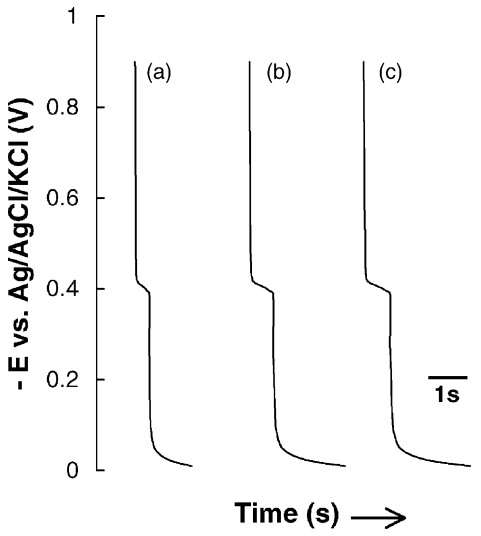

Fig. 1. Potentiometric stripping curves of one real sample (b), 5 μg/dm^3 (a), and 15 μg/dm^3 (c) standard lead solution. Conditions: depsition potential −0.96 V vs. Ag/AgCl, KCl (3.5 mol/dm^3); electrolysis time 240 s; solution stirring rate 4000 rpm; inverse current 1.2 μA. Curves are offset for clarity.

Table 3
Lead contents in the teeth extracts determined by the PSA-i_R and FAAS methods

Sample no.	Mass of sample (g)	Lead concentration (μg/dm^3)		C_V (%)	δ_T (%)
		PSA-i_R	FAAS		
I	0.70	12.87	12.60	2.47	2.14
II	0.64	12.95	12.50	3.14	3.60
III	0.68	18.12	18.40	7.42	−1.52
IV	1.03	13.36	12.70	4.82	5.20
V	1.33	13.73	13.50	4.12	1.71

The potentiometric stripping curves of one sample together with the curves for the 5 and 15 μg/dm^3 standard lead solutions are given in Fig. 1.

The lead concentration was calculated according to the following calibration curve:

$$C_m = 29.41 \cdot \tau_{ox} - 6.35; \ (r = 0.993)$$

which was obtained for the concentration range from 10 to 20 μg/dm^3 under above-mentioned conditions of analysis. The results obtained by the PSA-i_R method and the results of the reference FAAS method are given in Table 3 together with the results of the relatf the two methods and the coefficients of variation.

The results of the comparative analysis showed a very good agreement between the PSA-i_R and the FAAS method. On the basis of the values of the coefficient of variation, it can be concluded that it is possible to apply the calibration curve method for obtaining more reproducible values than by the standard addition method where the deviations are somewhat greater. Hence, the calibration curve method is proposed as the standard method for the determination of lead in the human teeth in dental research.

4. Conclusion

The results given in this paper show that the PSA-i_R can be successfully applied for the soluble lead determination in the human teeth. The sensitivity and reproducibility of the PSA-i_R method for the analysis of the soluble lead in teeth were determined. All the results were confirmed by the parallel FAAS analysis.

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